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RESOLUTION FOR CONDITIONS FOR APPROVAL OF THE URANYL NITRATE HEXAHYDRATE REMOVAL ACTION WORK PLAN

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LETTER

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Department of Energy
Fernald Environmental Management Project
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JAN 12 1995

DOE-0400-95

Mr. James A. Saric, Remedial Project Director
U.S. Environmental Protection Agency
Region V - 5HRE-8J
77 W. Jackson Boulevard
Chicago, Illinois 60604-3590

Mr. Tom Schneider, Project Manager
Ohio Environmental Protection Agency
401 East 5th Street
Dayton, Ohio 45402-2911

Dear Mr. Saric and Mr. Schneider:

RESOLUTION FOR CONDITIONS FOR APPROVAL OF THE URANYL NITRATE HEXAHYDRATE REMOVAL ACTION WORK PLAN

References:

1. Letter, J.R. Craig, DOE-FN, to J.A. Saric, U.S. EPA, and T. Schneider, OEPA, "Revised Uranyl Nitrate Hexahydrate Removal Action Work Plan," dated September 2, 1994.
2. Letter, J.A. Saric, U.S. EPA, to J.R. Craig, DOE-FN, "Removal Action 20 Work Plan, Revision 1," dated November 28, 1994.
3. Letter, J.A. Saric, U.S. EPA, to J.R. Craig, DOE-FN, "Approval of the Removal Action 20 Uranyl Nitrate Neutralization Project Work Plan," dated August 9, 1994.
4. Letter, T.A. Schneider, OEPA, to J.R. Craig, DOE-FN, "DOE FEMP MSL #531-0297 RA 20 Uranyl Nitrate Neutralization Project Work Plan," dated October 6, 1994.

This letter documents resolution of outstanding conditions for approval of the Removal Action Work Plan for the Uranyl Nitrate Hexahydrate (UNH) Neutralization Project (Reference 1). In Reference 2, the United States Environmental Protection Agency (U.S. EPA) restated two of the conditions stated in their conditional approval of the work plan (Reference 3). Stoichiometric information regarding the neutralization process was faxed to the U.S. EPA during the telephone conference on December 8, 1994; the U.S. EPA subsequently indicated that the information adequately resolved the first comment in Reference 2.

The second comment stated in Reference 2 regarded justification for the number

of samples specified by the work plan to confirm the filter cake generated by the neutralization project was, in fact, non-Resource Conservation And Recovery Act (RCRA) hazardous. As discussed in our most recent telephone conversation with the U.S. EPA and information provided by the enclosure of this letter, in order to resolve the U.S. EPA's second condition for approval of the work plan, we will take a minimum of two samples per batch for all batches, rather than for only the first seven batches.

In Reference 4, the Ohio Environmental Protection Agency (OEPA) OEPA conditionally approved the work plan contingent upon the schedule for neutralization of the UNH being included as part of the work plan. The current schedule was for neutralization to begin January 17, 1995, and be completed by September 29, 1995, however, will not be met due to problems with the project. I will provide a schedule after a complete review of the design is completed and a comprehensive Critical Path Method (CPM) schedule has been developed for the UNH Neutralization Project.

If you or your staff have any questions or require additional information concerning this matter, please contact Chris White at (513) 648-3172.

Sincerely,

for Jack R. Craig
Director

FN:White

Enclosures: As Stated

cc w/enc:

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FEMP SAMPLING APPROACH FOR UNH FILTER CAKE

The batch processing of UNH solution will generate two distinct waste streams: 1) aqueous filtrate, and 2) filter cake. Characterization of the filter cake to be generated from the UNH solution will draw heavily on the successful work completed to date. Work completed to date includes bench scale testing and the processing of the first 20,000 gallons of UNH at the FEMP. This work demonstrated the effectiveness of the process in producing a filter cake that is homogeneous in nature (i.e., low sample variability) and which does not leach RCRA metals at levels of concern (i.e., far below regulatory limits).

It is anticipated that the processing will require 30 to 50 individual batches to treat the remaining 200,000 gallons of UNH solution. The filter cake generated from each batch processed will be sampled and analyzed to verify that the process continues to perform as expected and to establish a correlation between the feed materials, processing conditions and the final waste product. Because each batch is extremely well mixed, only two samples will be required from each batch processed. Taking two samples allows basic statistics such as the mean (arithmetic average), variance and confidence limit to be calculated. If sample results show either higher variability or higher levels of RCRA metals leaching from the waste, then additional samples will be taken from the filter cake prior to processing for disposal. Requirements for additional samples will be based on EPA's SW-846 "Test Methods for Evaluating Solid Waste, Physical/Chemical Methods", Chapter 9, Equation 8.

The sampling approach for UNH filter cake is based on two well supported assumptions: 1) the neutralization/precipitation process produces a filter cake which is homogeneous, and 2) the resultant waste matrix is such that RCRA metals are not easily leached. There is a long history of industrial application of these processes to acidic and metal bearing waste streams in the metal plating and polishing, steel and nonferrous metals, mining, and electronics industries. For the UNH waste stream in particular, data collected during bench scale testing and from processing of the first 20,000 gallons of UNH solution at the FEMP demonstrate the effectiveness of the process.

The UNH solution is processed batch-wise allowing for maximum control over the process. The feed materials (UNH solution, dilution water, and magnesium oxide) are mixed in feed tanks F1-25 and F1-26 where the acid is neutralized and metal oxides/hydroxides formed over an 18 - 24 hour period. Constant mixing of the feed tank throughout this process ensures a well mixed, homogeneous slurry. The slurry is then pumped and filtered on the EIMCO rotary vacuum filters providing physical separation of the filter cake from the filtrate. This process generates a filter cake that, like its parent slurry, is homogeneous.

The low leachability of metals from the filter cake is a result of two contributing factors. First, the primary reason the metals ended up coming out of solution in the first place is because in their oxide and hydroxide forms they are not very soluble. Second, the weak glacial acetic acid leaching solution used in the Toxicity Characteristic Leaching Procedure (TCLP) tends to be neutralized by excess hydroxides in the filter cake reducing the aggressiveness of the leaching solution.

Thus, by design, the UNH neutralization and precipitation process generates a filter cake that is homogeneous with low leachability of RCRA metals. Analytical

results from bench scale testing and two sets of sampling for the filter cake generated from processing the first 20,000 gallons of UNH support these expected results (i.e., homogeneous, low leachability). Results from these sampling events is provided in Attachments 1, 2, and 3. For each data set, the following is discussed: purpose/approach of the sampling; results; mean and variance; and conclusions.

Chapter 9 of EPA's SW-846 "Test Methods for Evaluating Solid Waste, Physical/Chemical Methods" recommends that with an initial estimate of the mean and variance Equation 8 be used to determine the appropriate number of samples to collect under a simple random sampling scheme to adequately characterize the waste. Given the low mean and small variance obtained from the sampling of filter cake from the UNH processed last year, Equation 8 returns an extremely low number of samples required to characterize the remainder of the waste stream (less than 1). The approach outlined above utilizes a judgmental sampling scheme appropriately tailored to the batch-wise processing of the UNH solution and results in the collection of more samples than would be dictated by the application of Equation 8. Example calculations for UNH filter cake statistics are provided in Attachment 4.

In addition to the statistics completed on sampling results for each individual batch, a statistical analysis has been completed to compare intra-batch variability. The correlation is drawn between feed materials and analytical results for the final filter cake product. With the mix time and pH of the neutralized solution controlled, the leachable (TCLP) concentration of RCRA metals in the filter cake appear to be fairly independent of initial starting total concentration in the UNH solution. A fitted regression line with an 80% confidence interval (90% confidence limit) about the mean response has been generated to serve as a "control chart" for the process. These charts for chromium and barium are provided in Attachment 5. Note that the four data points in this analysis and that the data points are based on results from the initial UNH processing and from the bench scale testing. Analytical results from each batch processed will be compared to these charts to ensure that the process continues to operate as expected.

The FEMP initially proposed eliminating sampling of filter cake from each batch after the first seven batches were processed if a strong correlation could be formed between feed materials and final filter cake leachability. This approach sought to strike a balance between the cost and benefit of continuing to pull two samples from the filter cake generated from each batch. Based on comments from USEPA, the FEMP committed to continuing to pull two samples from the filter cake from each batch processed.

All sampling and analysis will be completed in accordance with the FEMP Sitewide CERCLA Quality Assurance Project Plan (SCQ). Sampling will be conducted following the Prototype Sampling and Analysis Plan (SAP) for containerized waste. As required by the Prototype SAP, a Project-Specific Sampling and Analysis Plan (PSAP) will be generated for this sampling effort specifying the detailed information required for each sampling event (e.g., drum numbers, number of samples required, parameters for analysis). The physical sampling will be conducted following FERMCO procedure 20-C-806 "Sampling of Drummed Material for Hazard Identification". Analytical results will be summarized and included in

the characterization file for this waste stream (Material Evaluation Form (MEF) Number 1186).

The characterization approach outlined above is consistent both with characterization approaches utilized in the chemical processing industry. This approach is also consistent with approaches utilized by USEPA in sampling and analysis efforts supporting hazardous waste listing program determinations (see the Background Information Documents for any number of HSWA required listing determinations by EPA).

Attachment 1.0
Bench Scale Test Report

1. Purpose/Approach

Bench test work was conducted in support of the UNH project for three purposes: 1) to characterize the contents of the individual UNH tanks, 2) to investigate the possible treatment conditions and verify that the treated material would meet existing discharge/disposal criteria, and 3) to recommend treatment conditions for the UNH inventory.

With respect to the second item, the bench scale work demonstrated that: 1) MgO was the preferred reagent for neutralization/precipitation due to the better filterability of the precipitated solids, 2) the rates of neutralization/precipitation are sufficient to make ambient processing practical, and 3) at the precipitation conditions necessary for filtrate discharge (i.e., pH > 7.0) the uranium and heavy metal residuals will be acceptable for both filtrate discharge and filter cake disposal.

UNH solutions were processed in jar tests on the lab bench to simulate the intended UNH treatment process. UNH solution was first diluted to reach acid strength of less than 1 N and U concentration of less than 100 g/l. MgO was then added to the stirred system and allowed 18 hour contact time to carry out neutralization. The neutralized UNH solution was then filtered on filter paper precoated with diatomacious earth to simulate performance of the EIMCO filters. Three samples of the resultant filter cake were submitted for TCLP analysis consistent with EPA Method SW-846 1311. Those three samples were believed to have the highest concentration of RCRA metals based on the original UNH characterization. The TCLP involves contacting a 100 g sample of solids with up to 2 liters of dilute acetic acid (pH ~5.0) for a period of 24 hours. At the conclusion of the test, an aliquot of the leachate is filtered and analyzed for the presence of RCRA metals.

2. Results

Results from the TCLP analysis of three different filter cakes generated from bench scale jar tests are summarized below. Note that the final pH of the UNH solution was only taken to a pH of between 5.0 and 6.0 which, as expected, somewhat reduces the effectiveness of the neutralization/precipitation process.

	UNH Solution (ppm)		TCLP Filter Cake (ppm)	
Tank Number	Ba	Cr	Ba	Cr
D1-1/10[1]	89.2	734.3	0.349	0.272
F1-25/26[1]	92.6	215	0.253	0.053
F1-1	412.5	344.3	0.313	0.454

[1] test solution was a mixture of sample from the two tanks.

3. Mean and Variability

The mean constituent concentration and variance *across all three initial UNH solutions concentrations* are summarized below.

constituent	$\bar{x}$ (ppm)	s
Ba	0.31	0.05
Cr	0.26	0.2

4. Conclusions

By only taking the final pH of the solution to pH between 5.0 and 6.0 the metals were not bound in the filter cake as strongly as they would have been if the final pH of the solution were taken to pH > 7.0 as is required when the UNH is processed. Neutralization to pH > 7.0 will more strongly bind the RCRA metals in the filter cake matrix.

Mean concentrations of RCRA metals in the filter cake appear to be somewhat independent of starting concentration in UNH solution. This is because the RCRA metals are all at relatively low concentrations compared with the uranium in the solution and filter cake.

First Sampling for Filter Cake from Processing 20,000 gal UNH

1. Purpose/Approach

In the fall of 1992, the first 20,000 gallons of UNH solution were processed to yield over 500 drums of filter cake. For Materials Control and Accountability (MC&A) purposes the drums were grouped into 60 drum lots as they were generated. One composite sample was collected from each 60 drum lot. The composite sample was comprised of a subsample from every tenth drum of the lot. Each composite sample was submitted to the laboratory for analysis immediately following collection. Eight samples were collected in this manner. Results from the first seven samples are summarized below. Laboratory analysis was not completed for the eighth composite sample based on results returned from the first seven samples.

2. Results

The results from the first seven samples for the two RCRA metals of concern are summarized below.

TCLP Filter Cake Results	
Ba (ppm)	Cr (ppm)
0.369	0.017
<0.2	<0.01
0.4597	<0.01
0.3596	<0.01
<0.2	<0.01
0.3423	<0.01
0.3291	<0.01

3. Mean and Variability

The mean constituent concentration and variance *across the seven composite samples* are summarized below.

constituent	$\bar{x}$ (ppm)	s
Ba	0.3	0.139
Cr	0.007	0.005

NOTE: 1/2 the DL used for value in computing the mean and variance

4. Conclusions

These results indicate that when final slurry pH is taken to pH > 7.0 the RCRA metals are bound up extremely well in the filter cake. The filter cake also appears to be very homogeneous across lots based on the variability from the

composite samples. However, the compositing may mask some degree of variability on a drum-by-drum basis.

Attachment 3.0 1/1
Second Sampling for Filter Cake from Processing 20,000 gal UNH

1. Purpose/Approach

To ensure that the characterization package for the UNH filter cake met the Waste Acceptance Criteria for NTS, the filter cake was resampled in the spring of 1994. This second sampling approach utilized a simple random sampling scheme using a random number generator to select the drums to be sampled. The second sampling event did not use composite sampling but selected an individual sample from each drum selected. This approach was taken to ensure that each drum had an equal chance of being sampled and that intra-drum variability was not masked by using composite samples. Four samples were collected using this approach.

2. Results

The results from the four random samples for the two RCRA metals of concern are summarized below.

TCLP Filter Cake Results	
Ba (ppm)	Cr (ppm)
0.777[1]	0.0359[1]
1.13	0.0107
0.471	0.0604
<0.2	0.0136

[1] Average of two field duplicates.

3. Mean and Variability

The mean constituent concentration and variance *across the four randomly selected samples* are summarized below.

constituent	$\bar{x}$ (ppm)	s
Ba	0.62	0.439
Cr	0.03	0.023

NOTE: 1/2 the DL used for value in computing the mean and variance

4. Conclusions

Once again, the results show that the RCRA metals of concern are bound up in the waste matrix in a form that does not leach RCRA metals at concentrations of concern. Based on the variability of the samples, the filter cake is once again demonstrated to be homogeneous in nature. As discussed above, these results are driven by the processing conditions and are expected to remain constant throughout the processing of UNH inventories at the FEMP.

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Attachment 4.0
CALCULATION SHEET
UNH Filter Cake Statistics

Sampling and analysis results for UNH filter cake sampled in the spring of 1994 (approximately 500 drums of UNH resampled to meet revised NTS Waste Acceptance Criteria (NVO-325 Rev. 1)).

Analytical results	
Ba	Cr
0.777[1]	0.0359[1]
1.13	0.0107
0.471	0.0604
<0.2	0.0136

[1] Average of two field duplicates.

NOTE: 1/2 the DL used for value in the statistics as an error minimizing approach.

Based on the data above:

terminology	symbol	Ba	Cr
number of samples	n	4	4
mean	$\bar{x}$	0.62	0.03
standard deviation of sample	s	0.439	0.023
standard error (standard deviation of mean of sample)	$s_{\bar{x}}$	0.22	0.0115
degrees of freedom	df	3	3
t-value	$t_{.20}$	1.638	1.638

Substituting into **equation 6 of SW-846 Chapter 9** one can form an 80% (two-tailed) Confidence Interval or 90% (one tailed) Confidence Limit:

In general:

$CI = \bar{x} \pm t_{.20} s_x$
where $s_x = s/\sqrt{n}$

For Ba:

CI = 0.62 ± 1.638(0.22)
CI = 0.62 ± 0.36
90% CL = 0.98 ppm

For Cr:

CI = 0.03 ± 1.638(0.0115)
CI = 0.03 ± 0.019
90% CL = 0.049 ppm

Using the estimates of the mean and variance from above, one can substitute into **equation 8 of SW-846 Chapter 9** to obtain an estimate of the appropriate number of samples to collect from a solid waste (financial constraints not considered):

In general:

$n = t^2_{.20} * s^2 / (RT - \bar{x})^2$ (where RT = regulatory threshold)

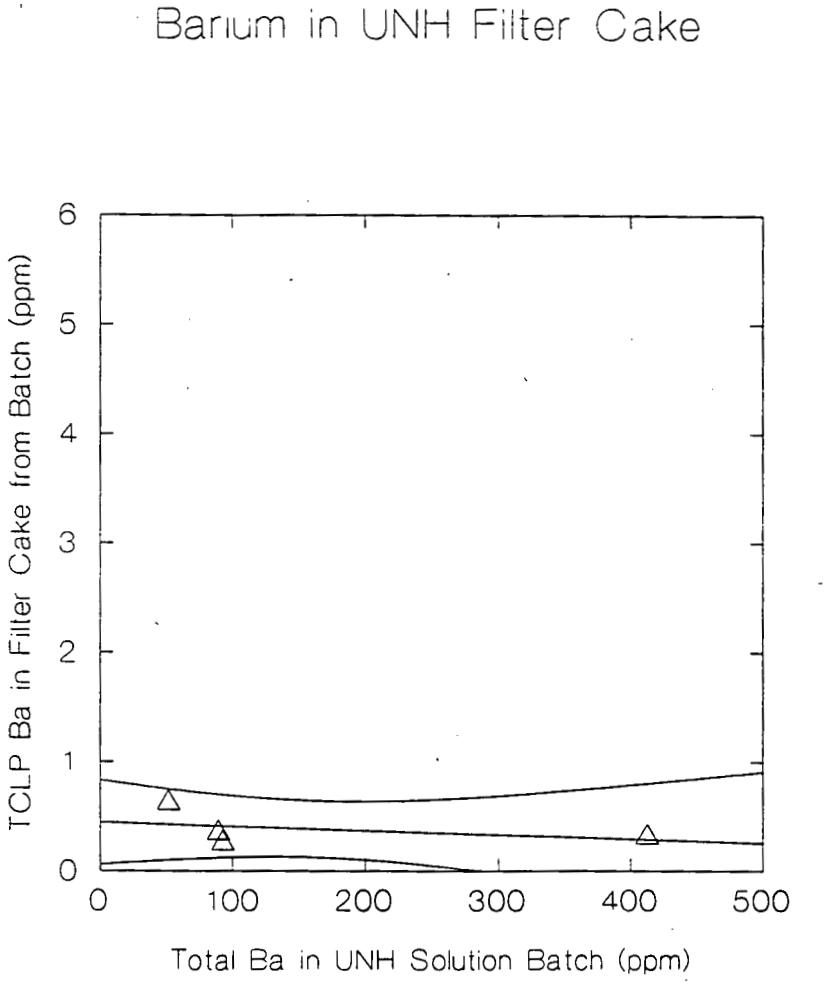
For Ba:

$n = (1.638)^2 * (0.439)^2 / (100 - 0.62)^2$
n = 5 EE-05 (or less than 1)

For Cr:

$n = (1.638)^2 * (0.023)^2 / (5 - 0.049)^2$
n = 5.8 EE-05 (or less than 1)

Attachment 5.0
Intra-batch Statistical Analysis of UNH Filter Cake



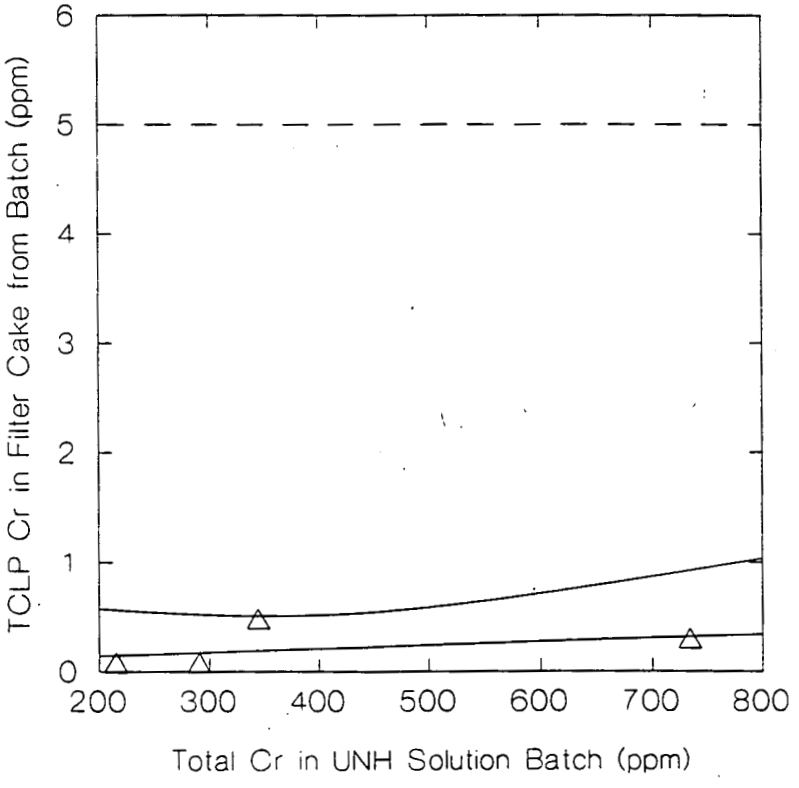
Data Used Above:

Tank Number	Total Ba in UNH Solution (ppm)	TCLP Ba in Filter Cake (ppm)
D1-1/10[1]	89.2	0.349
F1-25/26[1]	92.6	0.253
F1-1	412.5	0.313
F1-26	51.8	0.62

[1] test solution was a mixture of sample from the two tanks.

Attachment 5.0
Intra-batch Statistical Analysis of UNH Filter Cake

Chromium in UNH Filter Cake



— — - TC Regulatory Limit
——— 80% Confidence Interval for Mean Response

Data Used Above:

Tank Number	Total Cr in UNH Solution (ppm)	TCLP Cr in Filter Cake (ppm)
D1-1/10[1]	734.3	0.272
F1-25/26[1]	215	0.053
F1-1	344.3	0.454
F1-26	290	0.03

[1] test solution was a mixture of sample from the two tanks.